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An automatic stirring-assisted liquid–liquid microextraction system based on lab-in-syringe platform for on-line atomic spectrometric determination of trace metals

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ABSTRACT

A novel simple fully automatic on-line magnetic stirring-assisted liquid–liquid microextraction method, based on the lab-in-syringe (LIS) concept, has been developed as an alternative approach for sample pretreatment and atomic spectrometric assays. The analytical process includes the in-syringe reaction of the metal ion with the chelating reagent, the analyte micro-extraction and the subsequent transportation of the extractant to the detection system for electrothermal atomic absorption spectrometric (ETAAS) quantification. This novel platform has been demonstrated for trace silver determination in various types of water samples. The method is linear from 19 to 450 ng L^{-1} using a small volume of extraction solvent of 120 μL. The entire procedure is accomplished within 240 s resulting in a sampling frequency of 15 h^{-1}. The enhancement factor is 80, while the detection limit and the precision are 5.7 ng L^{-1} and 3.3%, respectively. The developed method was evaluated by analyzing standard reference materials and spiked water samples with satisfactory recoveries.

1. Introduction

Silver and silver containing compounds have numerous applications in industry and medicine as well as in the technology of cloud seeding. It is well known that silver ions have great potency as a microbial poison and are toxic to fish and many micro-organisms. Although they are relatively harmless to higher life forms including humans, bioaccumulation may be a concern for health issues [1]. Silver interacts metabolically with copper and selenium, preventing the uptake of these elements in the human body [2]. To prevent bacteria and algae from building up, colloidal silver is added in filters and water reclamation systems for purification in a view to avoid water chlorination. Concentrations in a range of 50–200 mg L^{-1} of silver are permitted to control antimicrobial activity with no risk to human life [3]. The ever increasing use of silver compounds in many aspects of human life has led to the need of trace silver determination in drinking water and environmental samples.

Although there is a continuous progress in the field of analytical techniques, there is still a great need for even higher sensitivity and interference elimination, due to the ultra-trace concentration levels of the metals and the high complexity of the matrix as well. A solution to the above issues is given by sample pre-treatment, in the context of preconcentration and separation, which is the most time consuming and error-prone step of the analytical process.

Following the modern trends in analytical chemistry, a renewed growth of interest in miniaturized systems has been experienced during the last decades, mainly by the development of microextraction techniques for separation and quantification, fulfilling the requirements of green analytical chemistry [4,5]. In this context, on-line liquid-phase microextraction (LPME) techniques, such as single drop microextraction (SDME) [6], hollow-fiber liquid phase microextraction (HF-LPME) [7], dispersive liquid–liquid microextraction (DLLME) [8–11] and liquid–liquid microextraction (LLME) achieved by the kinetic energy of either a magnetic stirrer [12] or by air-assistance [13], offer a great reduction in the volume of organic solvents as well as increased sensitivity due to the high ratio of donor to acceptor phase [14,15].

Flow analysis plays an important role on the minimization of reagent consumption and waste generation, as well as on the improvement of the analytical features such as precision and sampling rate. Toward the automation and miniaturization of the analytical systems, a simple and robust platform, the so-called lab-in-syringe (LIS), has been recently developed. The LIS system has increasing levels of functionality and versatility, facilitating the automatic sample and reagent manipulation [9,16,17]. This platform is based on an integrated micro-system consisted of a

multi-selection valve (SV) which is directly connected with a micro-syringe pump. In a fully automatic way, chemical reactions and various operations like extraction or dilution can take place inside the syringe barrel (SB) of the micro-syringe pump. The SB acts as an entirely closed reaction chamber, avoiding any possible interference from/to the environment or loss of the analyte.

The LIS system can be combined with various detectors. Lately, hyphenation of the LIS platform with atomic absorption spectrometry has been firstly reported by our group for vapor forming elements determination like mercury for cold vapor atomic absorption spectrometry [16] and for headspace single drop micro-extraction [17]. The LIS system has been also employed for some interesting designs in the field of automatic DLLME coupled with spectrophotometric detectors for organic [9,18] and inorganic compounds [19–21]. An inherent problem of a LIS–DLLME system is the fact that the formation of the cloudy solution cannot be achieved in the entire mass of the aqueous phase inside the syringe barrel, resulting in inefficient extraction [20]. An attempt for addressing this problem has been based on the use of a magnetic stirrer combined with the LIS system, which extends the dispersion of the organic phase into the aqueous phase. In this case, the separation of the two phases is time consuming.

In the present work, an alternative approach for efficient extraction has been proposed based on the avoidance of the "dispersion methodology" resulting in fast phase separation. A fully automatic lab-in-syringe platform for on-line magnetic stirring-assisted liquid–liquid microextraction (LIS-SA-LLME) has been developed for atomic spectrometric assays. To the best of our knowledge, this is the first reported combination of LIS-SA-LLME with ETAAS for trace metal determination. This customized design allows very fast phase separation and is amenable to the use of an organic solvent with density lower or higher than water. The proposed system was demonstrated for silver determination using diisobutyl ketone (DIBK) as an extraction solvent. All main factors were investigated and optimized. The method was evaluated by analyzing standard reference materials (SRM) and spiked environmental samples.

2. Experimental

2.1. Instrumentation and software

A Perkin-Elmer Model 5100 PC atomic absorption spectrometer (Perkin-Elmer, Norwalk, CT, USA, http://las.perkinelmer.com) with a Zeeman effect background correction and a transversely heated graphite tube atomizer (THGA), equipped with a AS-71 furnace autosampler and a circulating cooling unit, were employed throughout the measurements. Pyrolytically coated THGA graphite tubes (Perkin-Elmer) with an integrated L'vov platform were used. Argon 99.996% was used as the purge and protective gas. A Perkin Elmer Lumina™ single element hollow cathode lamp (HCL) for silver, operated at 10 W, was used as a light source. The wavelength was set at 328.1 nm resonance line and the monochromator spectral bandpass (slit) was 0.7 nm. The graphite furnace temperature/time program for silver determination in DIBK includes the preheating and drying steps at 90 and 110 °C, respectively, as well as a pyrolysis step at 500 °C, as summarized in Table 1. Integrated absorbance (peak area) was used for signal evaluation throughout the study.

A high precision bi-directional micro-syringe pump (MicroCSP-3000, FIAlab Instruments, Bellevue, WA) with overall dimensions $12 \times 5 \times 12$ cm ($H \times D \times W$), consisting of a glass syringe barrel with a capacity of 5000 μL and a nine-position Teflon/Kel-F selection valve directly connected on the top of the syringe barrel, was used for fluidic manipulation. The LIS system was interfaced

Table 1

Graphite furnace temperature program for silver determination in 35 μL of DIBK, without modifier.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (mL min^{-1})
Preheating	90	5	10	250
Drying	110	10	20	250
Pyrolysis	500	10	20	250
Atomization	1800	0	5	0
Cleaning	2100	1	2	250

with a personal computer and controlled by the FIAlab application software for windows v. 5.9.245 (http://www.flowinjection.com). The entire system was commanded by the computer of the FIAlab®-3000, as has been reported elsewhere [22].

An additional six-port two-position injection valve (IV) (LabPro, Rheodyne, USA) and a 35 μL polytetrafluoroethylene (PTFE) loop (L) were employed in order to deliver an accurate volume of the extract into the graphite furnace for atomization and quantification.

The PTFE tubing connecting the IV with FAAS was kept as short as possible in order to minimize the dead volume and the dispersion of the eluent.

A Metrohm (http://www.metrohm-autolab.com/) E649 magnetic stirrer was used for the effective mixing of the aqueous and organic phases facilitating the extraction.

An Orion EA940 pH-meter was used for pH measurements.

2.2. Reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany, http://www.merck.de). Ultra-pure quality water was used throughout which was produced by a Milli-Q system (Millipore, Bedford. USA, http://www.millipore.com). All standard solutions were prepared immediately before use, by stepwise dilution of 1000 mg L^{-1} Ag(I) stock standard solution in HNO$_3$ 0.5 mol L^{-1} (Merck Titrisol) to the required sub μg L^{-1} levels. The chelating agent, 0.3% (m/v) diethyldithiocarbamate (DDTC) solution was prepared by dissolving an appropriate amount of DDTC (Aldrich, www.sigmaaldrich.com/european-export.html) in water. Di-isobutyl ketone was used as an organic reagent. All glassware were rinsed with distilled water, decontaminated for at least 24 h in 10% (v/v) nitric acid solution and rinsed again five times with ultra-pure water.

Water samples like tap, river and seawater were collected from the area of Northern Greece (Thessaloniki, Axios river, Thermaikos gulf). All samples were filtered through 0.45 μm membrane filters, acidified to 0.01 mol L^{-1} HNO$_3$ (pH~2.0) and stored at 4 °C in acid-cleaned polyethylene bottles, in order to determine the "dissolved metal" fraction with the proposed method.

The standard reference materials NIST CRM 1643e (National Institute of Standard and Technology, Gaithersburg, MD, USA, http://www.nist.gov/) containing trace elements in water and IAEA-433 (International Atomic Energy Agency, IAEA) marine sediment were also analyzed. In case of IAEA-433, an amount of ca. 0.3 g was precisely weighed into sealed Teflon crucibles and wetted by nitric acid, followed by perchloric and hydrofluoric acids. The digestion procedure was carried out using a HNO$_3$–HClO$_4$–HF acid mixture in a volume ratio of 3:2:1 at 130–140 °C in a stainless-steel pressurized bomb according to the recommendations of the manufacture. After cooling the system, the digests were properly diluted in ultra-pure water and used for the analysis. Sediments were stored into the fridge until the analysis.